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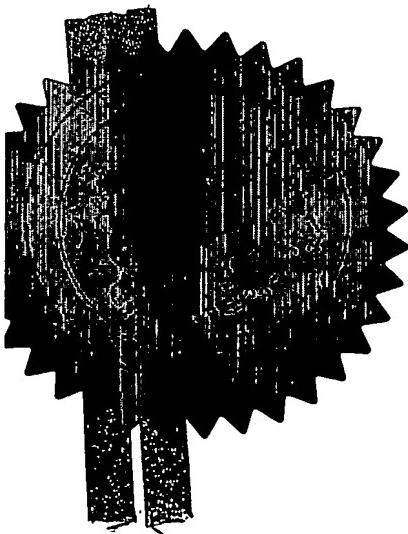
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*Stephen Hordley*

Dated 4 November 2004

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1. Your reference

SMC 60627/GB/P1

2. Patent application number

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0325324.2

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS

Patents ADP number *(if you know it)*

07764137001

If the applicant is a corporate body, give the country/state of its incorporation

GB

4. Title of the invention

Process for Producing Semiconducting Layers and Devices Containing the Same

5. Name of your agent *(if you have one)*

PARLETT, Peter Michael

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS  
United Kingdom

Patents ADP number *(if you know it)*

8463655001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number <i>(if you know it)</i>	Date of filing <i>(day / month / year)</i>
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing <i>(day / month / year)</i>
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

Yes

- any applicant named in part 3 is not an inventor, or
  - there is an inventor who is not named as an applicant, or
  - any named applicant is a corporate body.
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Claim(s)	22
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x2 J.W.

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Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

01

Request for substantive examination  
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Any other documents  
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11.

I/We request the grant of a patent on the basis of this application.

Signature *C. Stephed.* Date *28/10/03*  
Aveclia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Miss G. Terry 0161 721 1361/2

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SMC 60627

DUPLEXED

APPLICANTS

AVECIA LIMITED

TITLE

Process for Producing Semiconducting Layers and Devices Containing the Same

Process for Producing Semiconducting Layers and Devices Containing the Same

The present invention relates to a process for producing a semiconductor layer and an electronic device containing the same.

In multilayer organic electronic devices, for example organic field effect transistors (OFETs); organic light emitting diodes (OLEDs), organic solar cells and organic lasers, it may be desirable to include one or more organic semiconducting layers. The organic semiconducting layers may include, for example, light emitting layers or charge transporting layers for transporting holes and/or electrons.

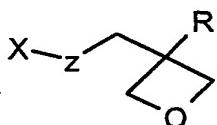
Such organic semiconducting layers may be deposited by vacuum deposition of active molecules i.e. those responsible for the electrical or light emitting properties (if the molecules are of low molecular weight) but as this is difficult and expensive or impractical with many high molecular weight materials, it is desirable to deposit them from a dispersion or solution by coating a substrate and evaporating them to leave a consolidated film. Often it is desirable to form multi-layered structures in such devices, however, if a preceding layer is soluble or dispersible in the same liquid used to deposit a subsequent layer, intermingling of the layers or erosion may occur thereby degrading the performance of the device.

It has been proposed to use "orthogonal" solvent/dispersant pairs to overcome this, i.e. solvents/dispersants are selected such that the solvent/dispersant used for the second etc. layer does not affect the first. However, a number of drawbacks exist. Such solvents may, because of the constraint in their choice, not be ideal for one or both layers and whilst some success may be obtained, it is still possible that some attack on the first layer may occur. If the layers in contact have similar solubility characteristics, for example because they are chemically similar, this approach may not be available. One solvent in such systems may be a polar liquid, water being typical, the other being non-polar. However, water is difficult to remove and if not removed may itself degrade the performance of the device.

A procedure has been disclosed in Muller et al, Synthetic Metals, 111-112 (2000) 31-34 in which a substrate is coated by spin coating with suitable cross-linkable active molecules and a photoinitiator, for example a photoacid catalyst, and the active molecules were then cross-linked by exposure to light of an appropriate wavelength. By this means a layer insoluble in a solvent used in the formation of a subsequent layer could be formed. Muller et al, Nature, 421 (2003) 829-833, apply a similar technique for forming RGB (red, green, blue) matrix displays by coating a substrate with a light emitting layer, cross linking areas of the layer by light passed through a mask, washing off the remainder of the layer and repeating the process with the two other light emitters onto different areas thereby forming pixels. Both of these references describe the use of oxetane groups of the active molecules for cross-linking. The use of such groups is said to lead to low shrinkage (<5%) of the films as described by Nuyken et al, Macromol. Symp., 107 (1996)

125-138. Shrinkage can lead to microcracks which can result in leakage currents and may ultimately cause short circuits.

WO97/33193 discloses arylamines having cross-linkable groups and films prepared from these materials and their use in electroluminescent and polymeric LEDs and as charge transport materials. That work does not claim or exemplify the use of oxetane units as the cross-linker group. WO02/10129 describes the use of low-molecular weight or polymeric compounds having at least one H group replaced by the oxetane unit of formula A and specifies



A.

the use of these materials in cross-linked films as potential emissive layers in LEDs but also discusses their potential use in other multi-layered structures such as organic lasers, solar cells, wave-guides or integrated circuits. Further examples of this type have been described by Meerholz in Macromolecular, Rapid Communications, 20 (2000) 224-228 and 21, (2000) 583-589 and also in Synth. Metals, 111-112 (2000) 31-34. These papers discuss the use of functionalised derivatives of N,N'-diphenyl-benzidine (TPD) which are linked together by non-conjugated groups to form the polymeric hole transport layer, this reduces the effectiveness of these materials as an organic semiconductor layer.

Meerholz et al. also describes an extension of this work in Chem. Phys. Chem., 4 (2000) 207 in which the substituted TPD units are linked by different numbers of benzene spacers between the nitrogen's (1 or 2), the monomers are then cross-linked using oxetane coupling units to form a non-conjugated polymeric structure as described above.

In the prior art, when polymers having a glass transition temperature  $T_g$  higher than the processing temperature are used, it can be difficult to achieve acceptable degrees of cross-linking. In order to maximise the extent of the cross-linking reaction it is desirable to carry out the process at temperatures near to the  $T_g$  of the polymer. In this invention, it is preferred to use processing temperatures as near as practicable to ambient and therefore, lower  $T_g$  compositions are preferred, for example of  $T_g$  60 to 100°C.

An object of this invention is to optimise the cross-linking of an organic semiconducting layer to give an insoluble layer which can be over-coated and in which shrinkage or microcracking is minimised. Desirably, the crosslinking should not significantly affect the charge mobility or the electrical properties.

The invention comprises a process of producing a semiconducting layer by coating a substrate with a mixture of a semiconducting material with a substance which results in

a Tg of the resulting mixture prior to crosslinking which is lower than that of the said material, and crosslinking the said material.

It is believed that this procedure permits the formation of less stressed layers in which microcracking is minimal (as assessed by optical means and by evaluation of electrical performance) even though the said substance may be consumed by reaction and/or evaporation and the layer may attain a higher Tg during the cross-linking reaction. Advantageously and unexpectedly, the use of the said substance does not significantly affect the electronic properties of the semiconducting material such as charge mobility.

The cross-linking is preferably carried out at a temperature near to the resulting Tg of the mixture preferably within  $\pm 20^{\circ}\text{C}$  thereof.

Preferably, the said substance itself contains functional groups capable of cross-linking the semiconducting material (i.e. crosslinkable groups).

Preferably, the semiconducting material contains functional groups capable of cross-linking it.

The semiconducting material preferably comprises an organic semiconducting material. The semiconducting material preferably comprises a semiconducting polymer, more preferably a  $\pi$ -conjugated semiconducting polymer, which has at least one cross-linkable group. The cross-linkable group is preferably linked to the semiconducting polymer by a linking group which comprises at least one, preferably at least four and more preferably at least six, for example six to twelve tetrahedral carbon atoms. The linking group may comprise, for example, a hydrocarbon or polyether chain. Preferably, the semiconducting polymer is crosslinked by reaction with the substance which, at the commencement of the crosslinking reaction, reduces the Tg of the semiconducting polymer. Preferably, the said substance also has a cross-linking functionality.

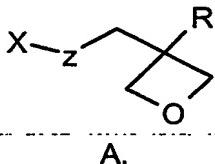
The  $\pi$ -conjugated semiconducting polymer preferably comprises, for example,  $\pi$ -conjugated units selected from at least one of poly (p-phenylene-vinylene), polyfluorene, poly-p-phenylene, polythiophene, polypyrrole or triarylamine units. The polymer preferably comprises 20 to 300 conjugated units. Preferably the  $\pi$ -conjugated semiconducting polymer comprises at least 5% and more preferably at least 40%, for example at least 90%, of triarylamine units (including their associated crosslinking groups) by weight. Suitably the  $\pi$ -conjugated semiconducting polymer consists only of triarylamine units (which may be substituted) and their associated crosslinking groups.

Blocks or units of  $\pi$ -conjugated semiconducting groups may be linked by non-conjugated linking groups if desired.

Whilst any one of many cross-linkable groups may be used, for example those described in WO97/33193, the disclosure of which is incorporated herein by reference, it is preferred, especially if cross-linking is performed photochemically, to use oxetane groups as these perform well in photochemical reactions and are helpful in minimising excessive shrinkage and cracking of the layer. Preferably, the crosslinkable groups

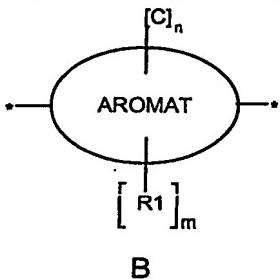
present on both the semiconducting polymer and the substance that lowers Tg comprise oxetane groups.

In this invention, a preferred cross-linkable group is an oxetane moiety of formula A where R is a straight chain, branched or cyclic alkyl, alkoxyalkyl or thioalkoxy group having from 1 to 20 carbon atoms each of which may be optionally substituted and in which one or more non-adjacent carbon atoms may be replaced by -O-, -S-, -CO-, -COO-, -O-CO-; -Z- is -O-, -S-, -CO-, -COO-, -O-CO- or -CR<sup>1</sup>R<sup>2</sup>- (where R<sup>1</sup> and R<sup>2</sup> each may be independently hydrogen, a hydrocarbyl or substituted hydrocarbyl group. -X- is a bivalent group -(CR<sup>1</sup>R<sup>2</sup>)<sub>n</sub>, where n is an integer from 1-20 and preferably 3 to 10 and where one or more non-adjacent carbon atoms may be replaced by -O-, -S-, -CO-, -COO-, -O- or CO.



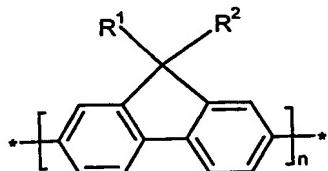
Thus, the X-Z- part of formula A constitutes a linking group as above which links the crosslinkable oxetane group to the semiconducting polymer.

The  $\pi$ -conjugated semiconductor polymer is preferably formed from one or more aromatic monomers (aromat) of which at least one monomer is substituted with one or more cross-linkable units C, preferably of type A, as shown in formula B, where n is 0 to 4. Each monomer unit may be optionally further substituted with one or more groups, R1, defined below where m=0-4. R1 may also be optionally substituted.



In formula B \* - can be a functional group which is polymerisable such as a reactive halogen Cl, Br, I or a boronic acid group, -B(OH)<sub>2</sub>, a substituted boronic ester -B(-OR<sup>1</sup>R<sup>2</sup>O) or a cyclic boronic ester.

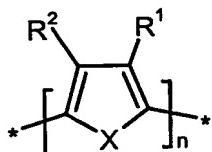
The aromat unit in formula B may itself comprise monomers where the number of repeat units, N, is N=1 or oligomers (including cooligomers) where N=2-15, preferably N=2-3, of one or more structures conforming to formulae 1 - 7:



5

Formula 1

where R<sup>1</sup> and R<sup>2</sup> may be independently a crosslinkable group (especially group A), H, optionally substituted alkyl, alkoxy, thioalkyl, acyl, aryl or substituted aryl, a fluorine atom, 10 a cyano group, a nitro group or an optionally substituted secondary or tertiary alkylamine or arylamine -N(R<sub>4</sub>)(R<sub>5</sub>), where R<sub>4</sub> and R<sub>5</sub> may each be independently represented by H, alkyl, substituted alkyl, aryl, substituted aryl, alkoxy or polyalkoxy groups; or other substituent. The alkyl and aryl groups may be optionally fluorinated.

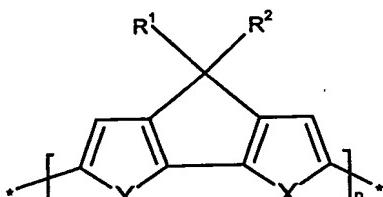


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Formula 2

in which X may be Se, Te or preferably O, S or -N(R)-, where R represents H; alkyl, substituted alkyl, aryl, or substituted aryl; R<sup>1</sup> and R<sup>2</sup> are as for formula 1.

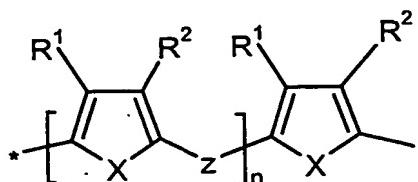
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Formula 3

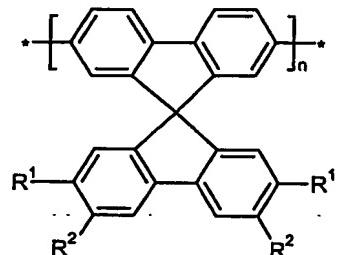
in which X is as for formula 2, R<sup>1</sup> and R<sup>2</sup> are as for formula 1.

25



Formula 4

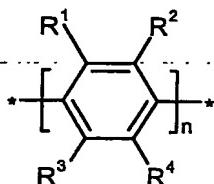
in which X is as for formula 2; R<sup>1</sup>, R<sup>2</sup> are as for formula 1 and Z represents -C(T<sub>1</sub>)=C(T<sub>2</sub>)-, -C≡C-, -N(R')-, -N=N-, (R')=N-, -N=C(R')-, T<sub>1</sub> and T<sub>2</sub> independently represent -H, Cl, F, -C≡N or a lower alkyl, R' represents -H, alkyl, substituted alkyl, aryl, or substituted aryl.



Formula 5

5

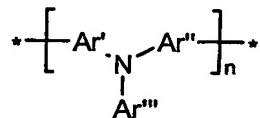
where R<sup>1</sup> and R<sup>2</sup> are as for formula 1.



Formula 6

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where R<sup>1</sup>-R<sup>4</sup> may be independently selected from the same list of groups as for R<sup>1</sup> and R<sup>2</sup> in formula 1.



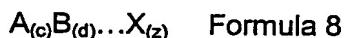
Formula 7

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Where the monomer is a tertiary amine monomer unit, the groups Ar', Ar'' and Ar''' being optionally substituted aryl groups in which the aryl groups Ar' and Ar'' may be phenylene groups. Ar''' may be optionally substituted (e.g. o- or p-substituted) with a cross-linkable group, especially group A, H, an alkyl, alkoxy, thioalkyl, acyl, aryl or substituted aryl, a fluorine atom, a cyano group or a nitro group.

20

Preferred classes of compounds for the semiconducting polymer include those containing conjugated repeat units. The semiconducting compound may be a homopolymer or copolymer (including a block-copolymer) of the general formula 8:



where A, B,...,X each represent a monomer unit and (c), (d),...(z) each represent the fraction of the respective monomer unit in the polymer, i.e. each (c), (d),...(z) is a value from 0 to 1 and the total of (c) + (d) +...+ (z) = 1. Examples of monomer units A, B,...X include units of formulae 1 - 7 given above. In the case of a block-copolymer, each monomer A, B,...X may be a conjugated oligomer or polymer comprising a number, for example 2 to 50, of the units of formulae 1-7. The conjugated repeat unit may, if desired, contain an emissive conjugated unit. The conjugated repeat units may contain a functionalised unit which can be used to modify the charge transport characteristics of the conjugated polymer and/or to provide a site to give cross-linking of the polymer chain to make it insoluble on irradiation with UV.

Preferably the ratio of the number of cross-linking groups in the polymer to the total number of monomer units in the polymer is 0.1 to 0.6 and more preferably 0.2 to 0.3. Any cross-linking groups of the substance which reduces the Tg of the polymer are additional thereto.

The quantity of the substance which reduces the Tg of the semiconducting material is preferably 5 to 60% by weight and preferably at least 10%, and more preferably at least 25%, still more preferably at least 40% by weight of the mixture of the said substance and the semiconducting material at the commencement of cross-linking. The Tg of the said mixture is preferably 60 to 100°C for example about 80°C.

The substrate may include any underlying layer, electrode or separate substrate such as silicon wafer or polymer.

Photochemical cross-linking may be catalysed by UV photocalysts, for example [4-{(2-hydroxytetradecyl)oxy}phenyl]iodonium hexafluoroantimonate. UV light frequencies of <380nm are suitably used.

Cross-linking is preferably carried out at a temperature of 40 to 120°C. If carried out below 100°C it is preferred to raise the temperature to 100 to 120°C at the end of the reaction to complete the cross-linking process and to anneal the film. Crosslinking may be effected by light, heat or both.

Preferably the mixture according to the present invention is deposited from a solvent. In this form of the invention, the solution is coated onto a substrate and the solvent is evaporated to form a layer or film. Preferably the composition and the compounds making up the composition are soluble in a wide range of organic solvents, e.g. without limitation, toluene, THF, ethyl acetate, dichloromethane, chlorobenzene, anisole and xylene. Thus, the composition may be applied to a substrate as part of a device manufactured by various types of solution coating. The composition can be applied to a substrate by a variety of coating or printing techniques such as dip coating, roller coating, reverse roll coating, bar coating, spin coating, gravure coating, lithographic coating (including photolithographic processes), ink jet coating (including continuous and drop-on-demand, and fired by piezo or thermal processes), screen coating, spray coating and web coating. A UV photoacid catalyst can be incorporated into the formulation at

between 0.01 and 5 wt% on the polymer. Suitable catalysts are well known in the field, see for example Nuyken et al., Macromolecular Symp. 107,125, 1996 and references therein. In this present invention a preferred catalyst is [4-{(2-hydroxytetradecyl)oxy}phenyl]iodonium hexafluoroantimonate. The resulting layer or film  
5 can be cross-linked by irradiating the film with UV light ( $\lambda < 380\text{nm}$ ) to form a solvent-insoluble layer which can subsequently be over-coated with other layers. Cross-linking may also be achieved by electron-beam lithography. This is particularly useful if a patterned layer is required, for example in order to produce pixels, but in other cases it may be desired to initiate the reaction by heat, free radicals or ionic mechanisms without  
10 the use of light (in which we include visible, infra red and ultra violet radiation).

Deposition of the layer on a substrate is preferably carried out by dissolving or dispersing a  $\pi$ -conjugated semiconducting polymer and the substance which reduces the  
Tg and optionally a catalyst for crosslinking in a suitable solvent dispersion, coating the  
15 substrate with the solution, preferably under an increased gravitational field, evaporating the solvent and cross-linking the resulting film. The cross-linking is preferably initiated by light.

The invention also provides an electronic device which comprises a layer prepared by the process. The device may comprise for example one of an OFET, OLED, organic solar cell photovoltaic device or organic laser.

20 The invention also provides a process in which a multilayer device is produced by forming a first layer which is a cross-linked semiconducting layer on a substrate by the process above and forming a second layer on the first layer by solution or suspension deposition of a further layer forming material wherein the first cross-linked semiconducting layer is insoluble in the solvent or suspending medium used to deposit the second layer.

25 The following are provided as examples of the present invention, but are non-limiting on the scope of the invention.

## Experimental Procedures

### 30 Part A: Synthesis of Monomers

All reactions were performed under anhydrous conditions and an atmosphere of nitrogen in flame-dried glassware unless otherwise stated. Yields refer to isolated materials, found to be homogeneous chromatographically (HPLC or GC) and spectroscopically ( $^1\text{H}$  NMR) unless otherwise stated. All NMR spectra were run with  
35  $\text{CDCl}_3$  as solvent unless otherwise stated.

Precursors**3-Ethyl-3-chloromethyloxetane (1)**

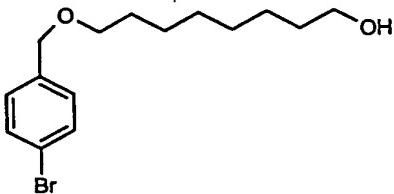
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This material was synthesised by a standard route, see H. Kenji, T. Koji and K. Takayoshi PCT JP2001-226364 and H.Kenji, T. Koji and K. Takajoshi PCT JP2001-122866.

A flame dried nitrogen purged 250ml flanged flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, thermometer and nitrogen inlet was charged with 3-Ethyl-3-hydroxymethyloxetane (9.50g, 81.8mmol), triethylamine (9.09g, 90mmol), and anhydrous N,N-dimethylformamide (65ml). The mixture was cooled to 0°C under an atmosphere of nitrogen and stirred for 30mins. Methane sulfonyl chloride (9.84g, 6.65ml, 86mmol) was added dropwise over 3 hours, keeping the temperature below 10°C. After this addition, the temperature of the mixture was raised to 20°C and the mixture stirred for 3 hours. The temperature of the reaction mixture was again raised to 85°C and the mixture stirred for a further 4 hours. After this time all triethylammonium chloride precipitate had reacted so that no cloudiness was evident in the reaction mixture.

Once the reaction was complete, water (250ml) was added to the reaction mixture and the resultant mixture extracted three times with toluene (120ml). The solvent was removed from the organic fraction *in-vacuo* and the crude residue purified by vacuum distillation [83-84°C at 35mm Hg] to yield the pure product. Yield = 3.542g, 32.2%. <sup>1</sup>H NMR: δ 4.43 (s, 4H, OCH<sub>2</sub>); 3.85 (s, 2H, CH<sub>2</sub>Cl); 1.85 (q, 2H, CH<sub>2</sub>); 0.95 (t, 3H, CH<sub>3</sub>).

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**8-(4-Bromobenzyl)octan-1-ol (2)**

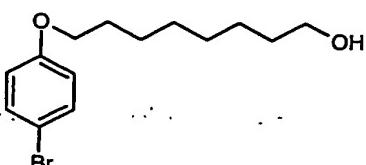
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In a flame-dried nitrogen-purged 250ml flanged flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, thermometer and nitrogen inlet was placed sodium hydride (4.50g, 0.11mol, 60% suspension in mineral oil, previously washed with hexane) suspended in dry N,N-dimethylformamide (150ml) under a nitrogen atmosphere. A solution of 1,8-octanediol (14.65g, 0.10mol) in dry N,N-dimethylformamide (100ml) was slowly added at 40°C, and the mixture stirred until evolution of hydrogen was complete. A solution of 4-bromobenzylbromide (25.00g, 0.10mol) in dry N,N-dimethylformamide (100ml) was the added simultaneously with potassium iodide (1.66g, 0.01mol). The

mixture was stirred at 90°C for 24 hours before being cooled to room temperature and diluted with diethyl ether (900ml). The organic solution was washed twice with distilled water (400ml), dried over magnesium sulfate and the solvent removed *in-vacuo*. The crude residue was purified by column chromatography [SiO<sub>2</sub>, toluene-ethylacetate 7:3].

5 Yield = 6.315g, 20.0%. <sup>1</sup>H NMR: δ 7.50, 7.20 (AA'BB', 4H); 4.45 (**s**, 2H, benzylic CH<sub>2</sub>); 3.65 (**t**, 2H, CH<sub>2</sub>); 3.45 (**t**, 2H, ethyl CH<sub>2</sub>); 1.55 (**m**, 4H, alkyl); 1.35 (**m**, 8H, alkyl).

### 8-(4-Bromophenoxy)octan-1-ol (3)



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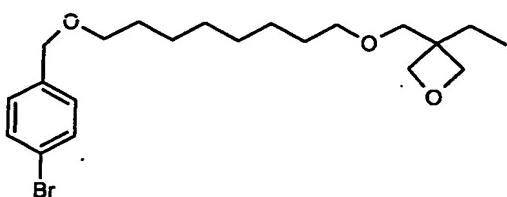
In a flame-dried nitrogen-purged 250ml flanged flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, thermometer and nitrogen inlet was placed 4-bromophenol (7.4456g, 0.043mol), 8-bromo-octan-1-ol (10.00g, 0.048mol) and dry N,N-dimethylformamide (100ml) under a nitrogen atmosphere. To this mixture was added potassium carbonate (26.3981g, 0.191mol) and the resultant mixture heated to 70°C under a nitrogen atmosphere and stirred overnight.

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After this time, the solvent was removed by first adding hexane and washing with water and then by removing the hexane *in-vacuo* to yield the crude product. The crude residue was purified by column chromatography [SiO<sub>2</sub>, hexane-dichloromethane 1:1]. Yield = 10.51g, 81.1%. <sup>1</sup>H NMR: δ 7.40, 6.75 (4H, AA'BB', phenyl); 5.30 (**s**, 1H, OH); 3.95 (**t**, 2H, CH<sub>2</sub>O); 3.65 (**t**, 2H, CH<sub>2</sub>O); 1.75 (**quintet**, 2H, CH<sub>2</sub>); 1.55 (**m**, 2H, alkyl); 1.45 (**m**, 4H, alkyl); 1.35 (**m**, 4H, alkyl).

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### 3-[8-(4-Bromobenzyloxy)octyloxymethyl]-3-Ethyloxetane (4)



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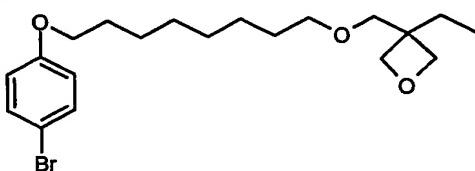
In a flame-dried nitrogen-purged 250ml flanged flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, thermometer and nitrogen inlet was placed sodium hydride (1.20g, 30mmol, 60% suspension in mineral oil, previously washed with hexane) suspended in dry N,N-dimethylformamide (70ml) under a nitrogen atmosphere. A solution of 8-(4-bromobenzyloxy)octan-1-ol (6.30g, 20mmol) in dry N,N-dimethylformamide (25ml) was slowly added at 40°C, and the mixture stirred until

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evolution of hydrogen was complete. 3-ethyl-3-chloromethyloxetane (2.963g, 22mol) was then added simultaneously with potassium iodide (0.166g, 1.0mmol). The mixture was stirred at 90°C for 24 hours before being cooled to room temperature and diluted with diethyl ether (700ml). The organic solution was washed twice with distilled water (180ml), dried over magnesium sulfate and the solvent removed *in-vacuo*. The crude residue was purified by column chromatography [SiO<sub>2</sub>, toluene-ethylacetate 9:1]. Yield = 5.4449g, 65.9%. <sup>1</sup>H NMR: δ 7.50, 7.10 (AA'BB', 4H, phenyl); 4.45 (d, 4H, CH<sub>2</sub>O); 4.35 (d, 2H, CH<sub>2</sub>O); 3.55 (s, 2H, CH<sub>2</sub>O); 3.45 (t, 4H, CH<sub>2</sub>O); 1.85 (q, 2H, ethyl); 1.60 (m, 4H, CH<sub>2</sub>); 1.35 (m, 8H, alkyl); 0.90 (t, 3H, ethyl).

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### 3-[8-(4-Bromophenoxy)octyloxymethyl]-3-Ethyloxetane (5)

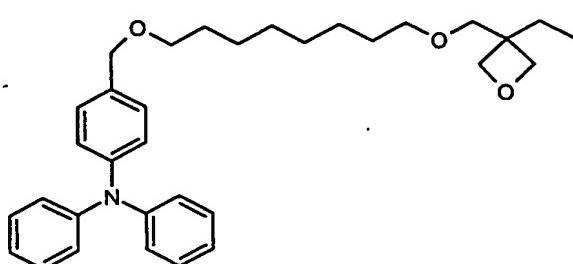


The same method as described to synthesise compound (4) was used in this preparation. Sodium hydride (2.0977g, 52.4mmol, 60% suspension in mineral oil, previously washed with hexane) suspended in dry N,N-dimethylformamide (120ml) was reacted with a solution of 8-(4-bromophenoxy)octan-1-ol (10.51g, 34.9mmol) in dry N,N-dimethylformamide (40ml) and 3-ethyl-3-chloromethyloxetane (5.170g, 38.4mol) with potassium iodide (0.290g, 1.745mmol). The crude residue was purified by column chromatography [SiO<sub>2</sub>, toluene-ethylacetate 9:1]. Yield = 2.8118g, 20.2%. <sup>1</sup>H NMR: δ 7.35, 6.75 (AA'BB', 4H, phenyl); 4.50 (d, 2H, CH<sub>2</sub>O); 4.40 (d, 2H, CH<sub>2</sub>O); 3.90 (t, 2H, CH<sub>2</sub>O); 3.55 (s, 2H, CH<sub>2</sub>O); 3.40 (t, 2H, CH<sub>2</sub>O); 1.75 (m, 4H, alkyl); 1.50 (m, 2H, alkyl); 1.35 (m, 8H, alkyl) and 0.90 (t, 3H, CH<sub>3</sub>).

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### {4-[8-(3-Ethyloxetane-3-methoxy)octyloxymethyl]phenyl}diphenylamine (6)



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In a flame-dried nitrogen-purged 250ml flanged flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, thermometer and nitrogen inlet was placed a solution of diphenylamine (2.231g, 0.0132mol), 3-[8-(4-bromobenzyl)oxy]octyloxymethyl]-3-ethyloxetane (5.44g, 0.0132mol) and sodium *tert*-butoxide (3.81g, 0.0397mol) in dry

outgassed toluene (80ml) under a nitrogen atmosphere. A solution of  $\text{Pd}_2(\text{dba})_3$  (120.9mg, 0.132mmol) and tris-*tert*-butylphosphine (160mg, 0.792mmol) in dry outgassed toluene (60ml). The mixture was stirred at 100°C for 24 hours until complete as shown by HPLC.

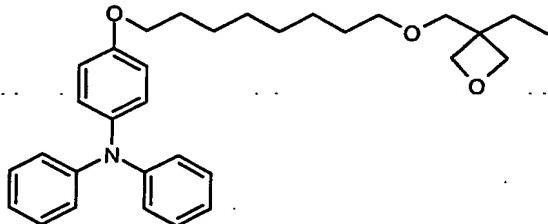
After this time the reaction mixture was cooled to room temperature and hexane (300ml)

5 was added. The solution was filtered and the solvent removed *in-vacuo* to yield an oil. The crude residue was purified by column chromatography [ $\text{SiO}_2$ , hexane – dichloromethane 1:1, gradient to dichloromethane – methanol 9:1]. Yield = 5.25g, 79.2%. Product was found to be pure by high performance liquid chromatography (HPLC).

<sup>1</sup>H NMR:  $\delta$  7.25 – 6.85 (*m*, 14H, phenyl); 4.45 (*m*, 4H,  $\text{CH}_2\text{O}$ ); 4.35 (*d*, 2H,  $\text{CH}_2\text{O}$ ); 3.55 (*s*, 2H,  $\text{CH}_2\text{O}$ ); 3.45

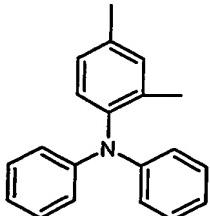
10 (*m*, 4H,  $\text{CH}_2\text{O}$ ); 1.80 (*q*, 2H,  $\text{CH}_2$ ); 1.6 (*m*, 4H,  $\text{CH}_2$ ); 1.35 (*m*, 8H, alkyl); 0.85 (*t*, 3H,  $\text{CH}_3$ ).

**{4-[8-(3-Ethyloxetane-3-methoxy)octyloxy]phenyl}diphenylamine (7)**



A similar method to that described for the synthesis of compound (6) was used in the preparation of this material, with diphenylamine (1.190g, 7.04mmol), 3-[8-(4-bromophenoxy)octyloxymethyl]-3-ethyloxetane (2.812g, 7.04mmol) and potassium *tert*-butoxide (2.370g, 21.12mol) in dry outgassed toluene (60ml) being reacted together with  $\text{Pd}_2(\text{dba})_3$  (65mg, 0.0704mmol) and 2-(di-*tert*-butylphosphino)biphenyl (126mg, 0.4224mmol) as catalyst in dry outgassed toluene (30ml). The crude oil was purified by column chromatography [ $\text{SiO}_2$ , hexane – dichloromethane 1:1, gradient to dichloromethane – methanol 9:1]. Yield = 2.73g, 79.4%. <sup>1</sup>H NMR:  $\delta$  7.20 – 6.85 (*m*, 14H, phenyl); 4.45 (*d*, 2H,  $\text{CH}_2\text{O}$ ); 4.35 (*d*, 2H,  $\text{CH}_2\text{O}$ ); 3.95 (*t*, 2H,  $\text{CH}_2\text{O}$ ); 3.55 (*s*, 2H,  $\text{CH}_2\text{O}$ ); 3.45 (*t*, 2H,  $\text{CH}_2\text{O}$ ); 1.75 (*m*, 4H,  $\text{CH}_2$ ); 1.6 (*m*, 4H,  $\text{CH}_2$ ); 1.45 (*m*, 2H,  $\text{CH}_2$ ); 1.35 (*m*, 6H, alkyl); 0.90 (*t*, 3H,  $\text{CH}_3$ ).

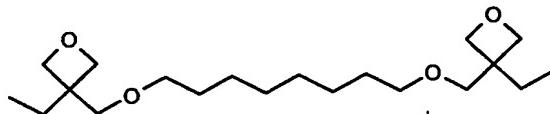
25 **(2,4-Dimethylphenyl)diphenylamine (8)**



A similar method to that described for the synthesis of compound (6) was used in the preparation of this material. A solution of diphenylamine (22.838g, 135.13mmol), 4-bromo-*m*-xylene (25.0g, 135.13mmol) and sodium *tert*-butoxide (38.92g, 405.39mmol) in dry outgassed toluene (300ml) were reacted together with Pd<sub>2</sub>(dba)<sub>3</sub> (1.237g, 1.3513mmol) and 2-(di-*tert*-butylphosphino)biphenyl (2.419g, 8.1078mmol) as catalyst in dry outgassed toluene (100ml). The crude oil was purified by column chromatography [SiO<sub>2</sub>, hexane]. Yield = 28.638g, 78.0%. <sup>1</sup>H NMR: δ 7.20 – 6.80 (*m*, 13H, phenyl); 2.35 (*s*, 3H, CH<sub>3</sub>); 1.95 (*s*, 3H, CH<sub>3</sub>).

10 **Synthesis of Tg-lowering Substance (reactive plasticiser)**

**1,8-Bis(3-Ethyloxetane-3-methoxy)octane (OCTYL DOX) (9)**

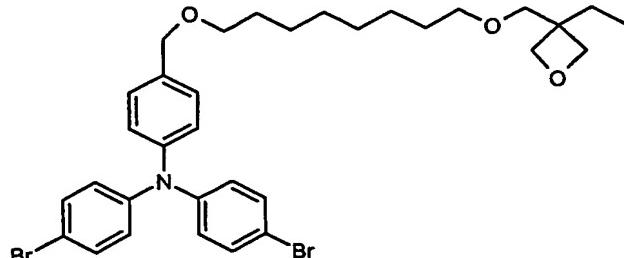


In a flame-dried nitrogen-purged 250ml flanged flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, thermometer and nitrogen inlet was placed sodium hydride (1.41g, 35.25mmol, 60% suspension in mineral oil, previously washed with hexane) suspended in dry N,N-dimethylformamide (200ml) under a nitrogen atmosphere. A solution of 1,8-octanediol (3.4318g, 23.5mmol) in dry N,N-dimethylformamide (70ml) was slowly added at 40°C, and the mixture stirred until evolution of hydrogen was complete. Next, 3-ethyl-3-chloromethyloxetane (7.0g, 51.85mol) was added simultaneously with potassium iodide (0.400g, 2.36mmol). The mixture was stirred at 90°C for 24 hours before being cooled to room temperature and diluted with diethyl ether (700ml). The organic solution was washed twice with distilled water (180ml), dried over magnesium sulfate and the solvent removed *in-vacuo*. The crude residue was purified by column chromatography [SiO<sub>2</sub>, toluene-ethylacetate 9:1].

25 Yield = 1.01g, 13.7%.

**Monomers**

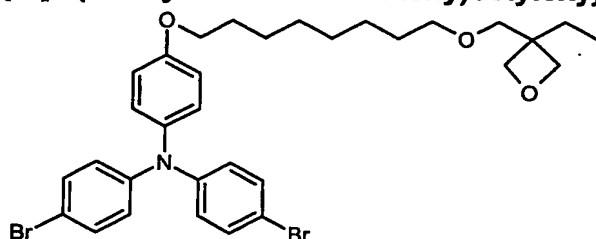
**Bis(4-Bromophenyl){4-[8-(3-Ethyloxetane-3-methoxy)octyloxymethyl]phenyl}amine (M1)**



In a flame-dried nitrogen-purged 250ml flanged flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, thermometer and nitrogen inlet was placed a solution of {4-[8-(3-Ethyloxetane-3-methoxy)octyloxy]phenyl}diphenylamine (5.25g, 10.5mmol) in dry N,N-dimethylformamide (30ml). The mixture was cooled to 0°C and a 5 solution of N-bromosuccinimide (3.738g, 21mmol) in dry N,N-dimethylformamide (20ml) was added. The mixture was stirred and allowed to warm to room temperature over 24 hours.

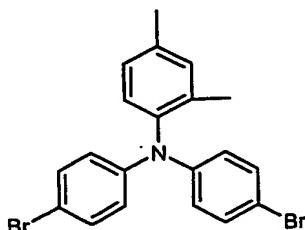
After this time the reaction mixture was poured into distilled water (100ml) and extracted three times with dichloromethane. The combined organic extracts were washed 10 with copious distilled water, dried over magnesium sulfate and the solvent evaporated *in vacuo* to yield the crude product. The product was then purified by flash column chromatography [SiO<sub>2</sub>; dichloromethane-hexane 9:1 gradient to dichloromethane-methanol 9:1] to yield the pure product. Yield = 3.10g, 45.0%. <sup>1</sup>H NMR: δ 7.30 – 6.75 (*m*, 12H, phenyl); 4.35 (*m*, 4H, CH<sub>2</sub>O); 4.25 (*d*, 2H, CH<sub>2</sub>O); 3.45 (*s*, 2H, CH<sub>2</sub>O); 3.35 (*m*, 4H, CH<sub>2</sub>O); 1.65 (*q*, 2H, CH<sub>2</sub>); 1.5 (*m*, 4H, CH<sub>2</sub>); 1.25 (*m*, 8H, alkyl); 0.80 (*t*, 3H, CH<sub>3</sub>). 15

#### Bis(4-Bromophenyl){4-[8-(3-Ethyloxetane-3-methoxy)octyloxy]phenyl}amine (M2)



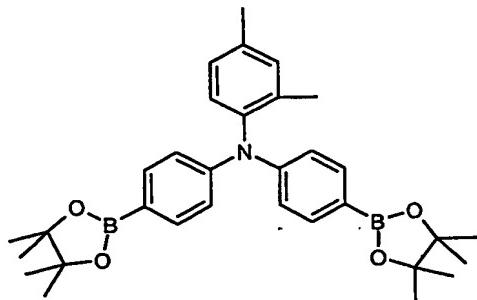
This monomer was synthesised by the same method as for M1. {4-[8-(3-Ethyloxetane-3-methoxy)octyloxy]phenyl}diphenylamine (2.73 g, 5.6mmol) in dry N,N-dimethylformamide (30ml) was reacted with N-bromosuccinimide (1.993g, 11.2mmol) in dry N,N-dimethylformamide (20ml). 20

The product was purified by flash column chromatography [SiO<sub>2</sub>; dichloromethane-hexane 9:1 gradient to dichloromethane-methanol 9:1] to yield the pure product. Yield = 2.07g, 57.3%. <sup>1</sup>H NMR: δ 7.30, 6.90 (*m*, 8H, AA'BB'); 7.05, 6.85 (*m*, 4H, AA'BB'); 4.45 (*m*, 2H, CH<sub>2</sub>O); 4.35 (*m*, 2H, CH<sub>2</sub>O); 3.95 (*t*, 2H, CH<sub>2</sub>O); 3.55 (*s*, 2H, CH<sub>2</sub>O); 3.45 (*t*, CH<sub>2</sub>O, 2H); 1.75 (*m*, 4H, alkyl); 1.60 (*m*, 2H, alkyl); 1.35 (*m*, 8H, alkyl); 0.85 (*t*, 3H, 0.85). 25

Bis(4-Bromophenyl)(2,4-dimethylphenyl)amine (M3)

This monomer was synthesised by the same method as M1. (2,4-dimethylphenyl)diphenylamine (17.39g, 0.064mol) in dry N,N-dimethylformamide (100ml) was reacted with N-bromosuccinimide (3.738g, 0.128mol) in dry N,N-dimethylformamide (100ml). The product was purified by flash column chromatography [SiO<sub>2</sub>, dichloromethane-hexane 1:1] to yield the pure product. Yield = 25.80g, 94.0%. <sup>1</sup>H NMR: δ 7.35 – 6.80 (m, 11H, phenyl); 2.40 (s, 3H, CH<sub>3</sub>); 2.05 (s, 3H, CH<sub>3</sub>).

10      **(2,4-Dimethylphenyl)-Bis(2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane)amine (M4)**



In a flame-dried nitrogen-purged 250ml three-necked flask fitted with a magnetic stirrer flea, septum cap, thermometer and nitrogen inlet was placed a solution of bis(4-bromophenyl)(2,4-dimethylphenyl)amine (12.50g, 0.029mol) and dry outgassed tetrahydrofuran (60ml). The solution was cooled to -78°C under a nitrogen atmosphere and n-butyl lithium (34.75ml, 0.087mol, 2.5M solution in hexanes) was added dropwise, maintaining the temperature at -78°C.

The resulting yellow solution was stirred at -78°C under nitrogen for 1 hour before 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17.75ml, 0.087mol) was added. The mixture was allowed to warm slowly to room temperature. The progress of the reaction was monitored by HPLC.

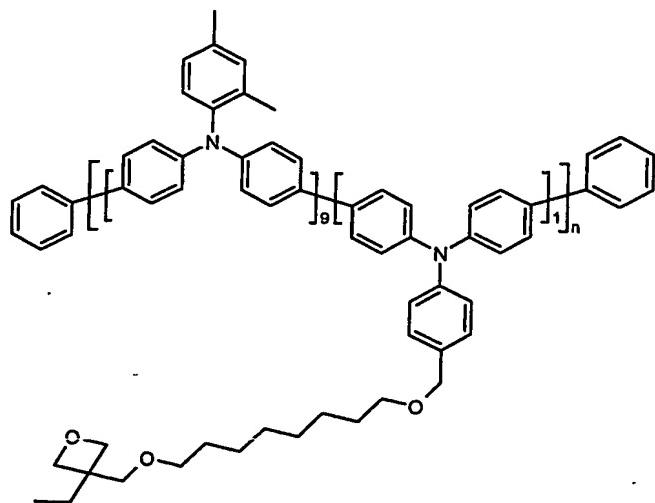
Upon complete reaction, the reaction mixture was evaporated *in-vacuo* and the residue dissolved in dichloromethane. The organic solution was washed three times with distilled water and dried over magnesium sulfate. The solvent was then removed *in-vacuo* to yield the crude product which was purified by flash column chromatography [SiO<sub>2</sub>, hexane – ethylacetate 95:5] and by repeated recrystallisation from hexane and methanol.

Yield = 8.43g, 55.4%.  $^1\text{H}$  NMR:  $\delta$  7.65 – 7.00 (m, 11H, phenyl); 2.35 (s, 3H,  $\text{CH}_3$ ); 2.05 (s, 3H,  $\text{CH}_3$ ); 1.40 (s, 24H, pinacol  $\text{CH}_3$ ).

### Part B: Synthesis of Polymers

5 Polymers were prepared by the widely known Suzuki coupling procedure, as described in "The Suzuki cross-coupling." by W.A. Herrmann, in Applied Homogeneous Catalysis with Organometallic Compounds (2nd Edition) (2002), 1 591-598, editors: B. Cornils and W.A. Herrmann, Wiley-VCH Verlag GmbH, Weinheim and by A. Suzuki in the Journal of Organometallic Chemistry (1999), 576(1-2), 147-168. Typical conditions  
 10 for the polymerization of boronic acid or ester derivatised monomers with bromine derivatised monomers has also been described in detail, see for example: "Transition metal-catalyzed-polycondensation and polyaddition" by W. Heitz, in Materials Science and Technology (1999), 20 (Synthesis of Polymers), 37-64, editor: A.D. Schlueter, Wiley-VCH Verlag GmbH, Weinheim, or in "The tenth anniversary of Suzuki  
 15 polycondensation" by A. D. Schlüter, in Journal of Polymer Science, Part A: Polymer Chemistry (2001), 39(10), 1533-1556.

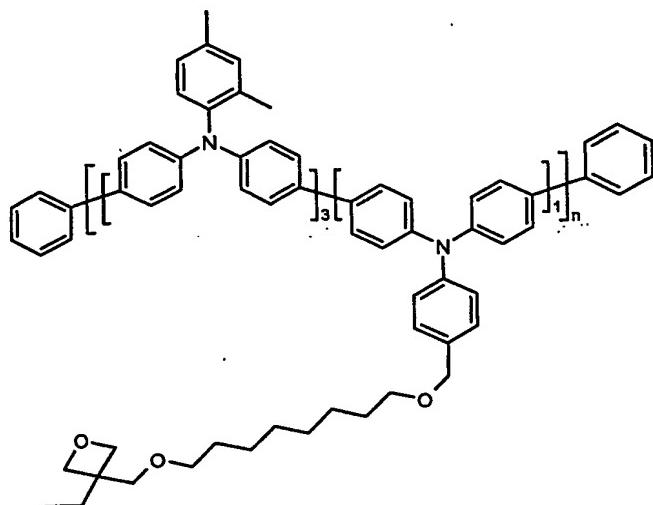
#### Polymer P1.



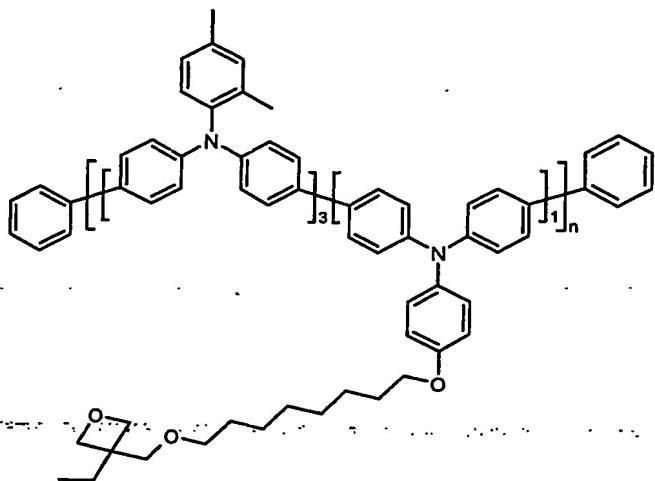
20 Copolymerisation of monomer M1 bis(4-bromophenyl){4-[8-(3-ethyloxetane-3-methoxy)octyloxymethyl]phenyl}amine monomer M3 bis(4-bromophenyl)(2,4-dimethylphenyl)amine, and monomer M4 (2,4-dimethylphenyl)-bis(2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane)amine was achieved by the methods described above. The quantities of monomers used were as follows: M3 bis(4-bromophenyl)(2,4-dimethylphenyl)amine (1.381g, 3.2mmol), M1 bis(4-bromophenyl){4-[8-(3-ethyloxetane-3-methoxy)octyloxymethyl]phenyl}amine (0.527g, 0.8mmol) and M4 (2,4-dimethylphenyl)-bis(2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane)amine (2.10g, 4mmol). The polymer was obtained as an off-white solid, in a yield of 2.10g, 89.4%.  $^1\text{H}$  NMR:  $\delta$  7.45 – 6.90 (m,

phenyl); 4.45 (*m*, CH<sub>2</sub>O); 4.35 (*m*, CH<sub>2</sub>O); 3.50 (*s*, CH<sub>2</sub>O); 3.40 (*m*, CH<sub>2</sub>O); 2.30 (*s*, CH<sub>3</sub>); 2.05 (*s*, CH<sub>3</sub>); 1.75 (*q*, CH<sub>2</sub>); 1.6 (*m*, CH<sub>2</sub>); 1.35 (*m*, alkyl); 0.90 (*t*, CH<sub>3</sub>). GPC (THF, 1mL/min, PL gel Mixed D): Mw = 41400g/mol; Mn = 8900g/mol.

## 5 Polymer P2.



Copolymerisation of monomer M1 bis(4-bromophenyl){4-[8-(3-ethyloxetane-3-methoxy)octyloxymethyl]phenyl}amine monomer M3 bis(4-bromophenyl)(2,4-dimethylphenyl)amine, and monomer M4 (2,4-dimethylphenyl)-bis(2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane)amine was achieved by the methods described above. The quantities of monomers used were as follows: M3 bis(4-bromophenyl)(2,4-dimethylphenyl)amine (0.8632g, 2.0mmol), M1 bis(4-bromophenyl){4-[8-(3-ethyloxetane-3-methoxy)octyloxymethyl]phenyl}amine (1,3180g, 2.0mmol) and M4 (2,4-dimethylphenyl)-bis(2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane)amine (2.10g, 4mmol). The polymer was obtained as an off-white solid. Yield 2.26g, 85.8%.  $^1\text{H}$  NMR:  $\delta$  7.45 – 6.90 (m, phenyl); 4.45 (m,  $\text{CH}_2\text{O}$ ); 4.35 (m,  $\text{CH}_2\text{O}$ ); 3.50 (s,  $\text{CH}_2\text{O}$ ); 3.40 (m,  $\text{CH}_2\text{O}$ ); 2.35 (s,  $\text{CH}_3$ ); 2.05 (s,  $\text{CH}_3$ ); 1.75 (q,  $\text{CH}_2$ ); 1.55 (m,  $\text{CH}_2$ ); 1.35 (m, alkyl); 0.85 (t,  $\text{CH}_3$ ). GPC (THF, 1ml/min, PL gel Mixed D):  $M_w$  = 35600g/mol;  $M_n$  = 10100g/mol.

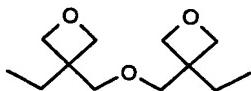
**Polymer P3.**

Copolymerisation of monomer **M2** bis(4-bromophenyl){4-[8-(3-ethyloxetane-3-methoxy)octyloxy]phenyl}amine monomer **M3** bis(4-bromophenyl)(2,4-dimethylphenyl)amine, and monomer **M4** (2,4-dimethylphenyl)-bis(2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane)amine was achieved by the methods described above. The quantities of monomers used were as follows: **M3** bis(4-bromophenyl)(2,4-dimethylphenyl)amine (1.09g, 2.53mmol), **M2** bis(4-bromophenyl){4-[8-(3-ethyloxetane-3-methoxy)octyloxy]phenyl}amine (2.07g, 3.20mmol) and **M4** (2,4-dimethylphenyl)-bis(2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane)amine (3.01g, 5.73mmol). The polymer was obtained as an off-white solid, in a yield of 3.68g, 96.8%. <sup>1</sup>H NMR: δ 7.40 – 6.80 (*m*, phenyl); 4.45 (*m*, CH<sub>2</sub>O); 4.35 (*m*, CH<sub>2</sub>O); 3.95 (*m*, CH<sub>2</sub>O); 3.55 (*s*, CH<sub>2</sub>O); 3.45 (*m*, CH<sub>2</sub>O); 2.35 (*s*, CH<sub>3</sub>); 2.05 (*s*, CH<sub>3</sub>); 1.85 (*m*, CH<sub>2</sub>); 1.55-1.25 (*m*, CH<sub>2</sub>); 0.85 (*t*, CH<sub>3</sub>). GPC (THF, 1ml/min, PL gel Mixed D): Mw = 27520g/mol; Mn = 11421g/mol.

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**Part C: Formulation Procedure**

The polymers **P1**, **P2** or **P3** were blended with the reactive plasticiser molecules bis[1-ethyl(3-oxtetanil)]methyl ether, **DOX** (Formula 9) (obtained from Toagosei), **OCTYL DOX** or a non-reactive plasticiser of ethylene glycol dimethyl ether, at a variety of ratios (Table 1). All ratios are weight to weight ratios. The reactive plasticiser **DOX** and unreactive plasticiser ethylene glycol dimethyl ether are commercially available. The reactive plasticiser **OCTYL DOX** was prepared as described in Experimental Part A: Synthesis of Monomers.



Formula 9: Commercially available DOX reactive plasticiser.

A photoacid catalyst such as the commercially available [4-(2-hydroxytetradecyl)oxy]phenylphenyliodonium hexafluoroantimonate was added to each formulation at, 5.0% weight to weight with respect to the total weight of the polymer/reactive plasticiser mixture. A solvent, typically toluene, was then added to the mixture such that it was dissolved in the ratio of one part into 99 parts of solvent. After mixing the formulation on a mechanical shaker for 20mins, each formulation was spin coated onto a quartz slide at 1000rpm for 20 seconds to give a film of approximately 100nm thickness. To ensure complete drying the sample was placed in an oven for 20 minutes at 100 °C. The UV-visible absorption spectrum of each film was then recorded using a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. The sample was then mounted in a quartz sample holder and a flow of nitrogen gas was passed over the film. The holder and sample were heated to, typically, 50 to 60°C before being irradiated with a standard laboratory UV source (254nm/360nm) for 3minutes. The film was then annealed at 100°C for, suitably, 10 minutes before being cooled to ambient temperature and washed with THF (2mL). To ensure complete drying the sample was again placed in an oven for 10 minutes at 100 °C. The UV-visible absorption spectrum of the film was then re-recorded and the intensity of the peak at  $\lambda_{max}$  noted. From comparison of the intensities of the spectra at the  $\lambda_{max}$  of the cross-linked and uncross-linked films, a measure of the quantity of polymer retained on the quartz slide may be estimated given that at a particular wavelength, light is absorbed by a material according to the quantity of material comprising the absorbing layer. Thus, the extent of crosslinking can be determined for each formulation (Table 1).

Table 1

25

Example Formulation	P1 (mg)	P2 (mg)	DOX (mg)	OCTYL DOX (mg)	Ethylene Glycol DME (mg)	% Cross-linked Polymer
1	0	80	80	0	0	97
2	80	0	80	0	0	50
3	0	80	0	80	0	93
4	80	0	0	0	0	8
5	0	80	0	0	0	41
6	0	75	25	0	0	73
7	80	0	0	80	0	59
8	0	25	75	0	0	87
9	0	80	0	0	80	84
10	0	75	28	0	0	78
11	75	0	30	0	0	33
12	80	0	0	0	80	41

Table 1: Example formulations of P1 and P2 with selected reactive plasticisers.

From Table 1 it is evident that significantly higher quantities of polymer are retained on the quartz test slides when reactive plasticisers such as DOX or OCTYL DOX are added to the formulation. When an un-reactive plasticiser such as ethyleneglycol dimethyl ether was used the amount of cross-linking was less but still improved compared to the case of no plasticiser. The best results were obtained when the weight to weight ratio of polymer to reactive plasticiser in the mixture was in the region of 50:50. The above results indicate that the reactive plasticisers are advantageous in these compositions. The polymer P2, having a ratio of the number of crosslinking groups to the number of monomers in the polymer of 0.25 is crosslinked better than P1 (ratio=0.1).

#### Part D: Characterisation of Thin Films

##### Glass Transition Temperatures

Measurement of the glass transition temperatures of example materials was carried out by differential scanning calorimetry (DSC).

Upon formulation of polymers P1 or P2 with, for example, the DOX reactive plasticiser, the T<sub>g</sub> of the resultant material is lowered from that of the pristine polymer. Upon crosslinking, the T<sub>g</sub> value would be expected to rise significantly as the material becomes a networked polymer, however this was difficult to observe by DSC.

##### Optical Microscopy of Films

Films were examined by optical microscopy under a crossed polariser prior to and after the crosslinking procedure described above. No evidence of shrinkage, microcracking or internally stressed films was observed in the films at up to 100x magnification.

##### Utility of Films in Electronic Devices

The formulated materials may be incorporated into electronic devices such as organic field effect transistors (OFETs) and organic light emitting diodes (OLEDs). As an example, a film of a formulation of the present invention was incorporated into an OFET device as described below.

##### Determination of the Field Effect Mobility

The field effect mobility of the materials was tested using the techniques described by Holland et al, J. Appl. Phys. Vol.75, p.7954 (1994).

In the following examples, a test field effect transistor was manufactured by using a Melinex polyester film substrate upon which were patterned Pt/Pd source and drain electrodes by standard techniques, e.g. shadow masking. The semiconductor formulation as described in experimental part C above, was spin coated onto the substrate at 1000 rpm for 20 s to yield a ~100 nm film. To ensure complete drying the sample was placed in an oven for 20 minutes at 100°C. The semiconductor formulation was then cross-linked by the method described in part C. A solution of an insulator material with a low frequency permittivity ( $\epsilon$ ) typically equal to 2.3 was then spin-coated onto the semiconductor giving a

thickness typically in the range 0.5  $\mu\text{m}$  to 1  $\mu\text{m}$ . The sample was placed once more in an oven at 100 °C to evaporate solvent from the insulator. A gold gate contact was defined over the device channel area by evaporation through a shadow mask. To determine the capacitance of the insulator layer a number of devices were prepared which consisted of a non-patterned Pt/Pd base layer, an insulator layer prepared in the same way as that on the FET device, and a top electrode of known geometry. The capacitance was measured using a hand-held multimeter, connected to the metal either side of the insulator. Other defining parameters of the transistor are the length of the drain and source electrodes facing each other ( $W=25 \text{ mm}$ ) and their distance from each other ( $L=100 \mu\text{m}$ ).

The voltages applied to the transistor are relative to the potential of the source electrode. In the case of a p type gate material, when a negative potential is applied to the gate, positive charge carriers (holes) are accumulated in the semiconductor on the other side of the gate insulator. (For an n channel FET, positive voltages are applied). This is called the accumulation mode. The capacitance/area of the gate insulator  $C_i$  determines the amount of the charge thus induced. When a negative potential  $V_{DS}$  is applied to the drain, the accumulated carriers yield a source-drain current  $I_{DS}$  which depends primarily on the density of accumulated carriers and, importantly, their mobility in the source-drain channel. Geometric factors such as the drain and source electrode configuration, size and distance also affect the current. Typically a range of gate and drain voltages are scanned during the study of the device. The source-drain current is described by equation 1.

$$I_{DS} = \frac{\mu W C_i}{L} \left( (V_G - V_0)V_{DS} - \frac{V_{DS}^2}{2} \right) + I_\Omega, \quad \text{eq. 1}$$

where  $V_0$  is an offset voltage and  $I_\Omega$  is an ohmic current independent of the gate voltage and is due to the finite conductivity of the material. The other parameters have been described above.

For the electrical measurements the transistor sample was mounted in a sample holder. Microprobe connections were made to the gate, drain and source electrodes using Karl Suss PH100 miniature probe-heads. These were linked to a Hewlett-Packard 4155B parameter analyser. The drain voltage was set to -20 V and the gate voltage was scanned from +20 to -60 V in 1 V steps. When  $|V_G| > |V_{DS}|$  the source-drain current varies linearly with  $V_G$ . Thus the field effect mobility can be calculated from the gradient of  $I_{DS}$  vs.  $V_G$  given by equation 2.

$$S = \frac{\mu W C_i V_{DS}}{L} \quad \text{eq. 2}$$

The field effect mobility of charge within formulated films before and after crosslinking were compared.

Example 1: An FET device comprising an uncross-linked film of a formulation of the present invention was constructed. The field effect mobility was of the material was found to be  $1.16 \times 10^{-3} \text{ cm}^2/\text{Vs}$  with transfer curve as shown in Figure 1.

- 5 Example 2: A FET device comprising a cross-linked film of a formulation of the present invention was constructed. The field effect mobility was of the material was found to be  $5.50 \times 10^{-4} \text{ cm}^2/\text{Vs}$  with transfer curve as shown in Figure 2.

10 Thus it can be observed that cross-linking the semiconductor formulation does not have substantial adverse effects on the device characteristics of FET devices.

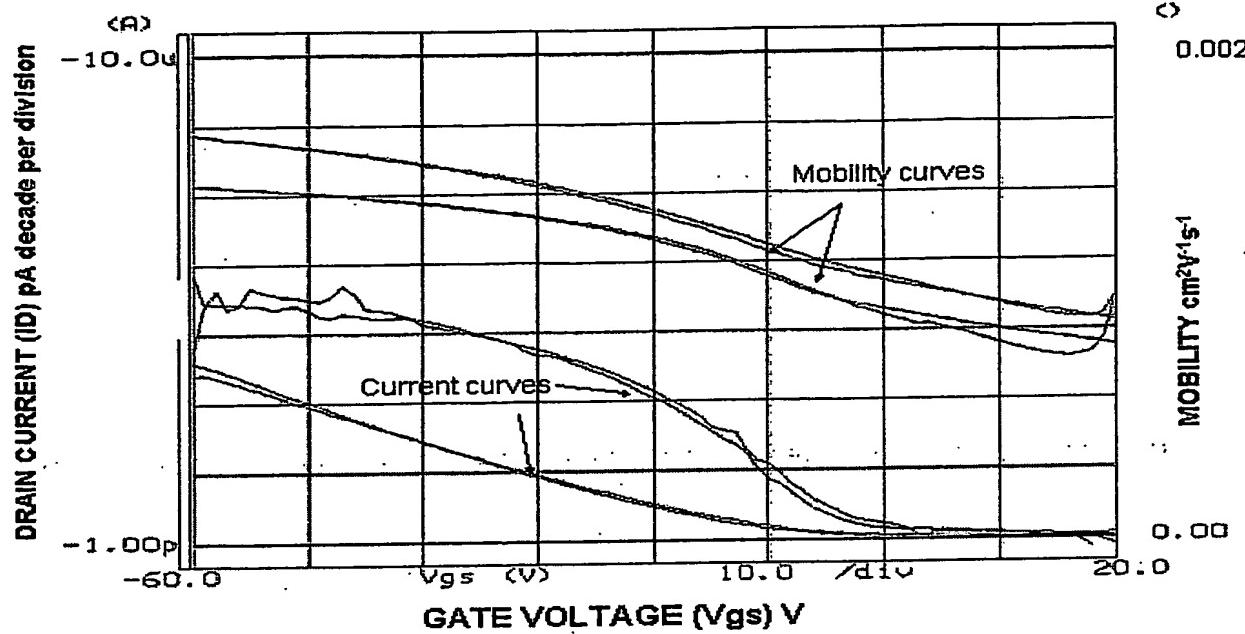
CLAIMS

1. A process of producing a semiconducting layer by coating a substrate with a mixture of a semiconducting material and a substance which results in a Tg of the resulting mixture which prior to crosslinking is lower than that of the said semiconducting material, and crosslinking the said semiconducting material.  
5
2. A process according to claim 1 in which the cross linking is carried out at a temperature near the resulting Tg of the mixture.
- 10 3. A process according to claim 1 or 2 in which the said substance itself contains functional groups capable of cross-linking the semiconducting material.
4. A process according to claim 1, 2 or 3 in which the semiconducting material contains functional groups capable of cross-linking the material.  
15
5. A process according to any one preceding claim in which the semiconducting material comprises  $\pi$ -conjugated semiconducting polymer which has at least one crosslinkable group.
- 20 6. A process according to claim 5 in which the  $\pi$ -conjugated semiconducting polymer comprises  $\pi$ -conjugated poly (p-phenylene-vinylene), polyfluorene, poly-p-phenylene, polythiophene, polypyrrole and/or triarylamine units.
- 25 7. A process according to claim 6 in which the  $\pi$ -conjugated semiconducting polymer comprises at least 5% and preferably at least 40%, more preferably at least 90% of triarylamine units including their associated crosslinking groups by weight.  
30
8. A process according to claim 7 in which the  $\pi$ -conjugated semiconducting polymer consists only of triarylamine units (which may be substituted) and associated cross-linking groups.
9. A process according to claim 8 in which the polymer comprises 20 to 300 conjugated units.  
35
10. A process according to any one preceding claim in which the functional cross-linkable groups comprise oxetane groups.
11. A process according to any one preceding claim in which the cross-linking is photochemically initiated.

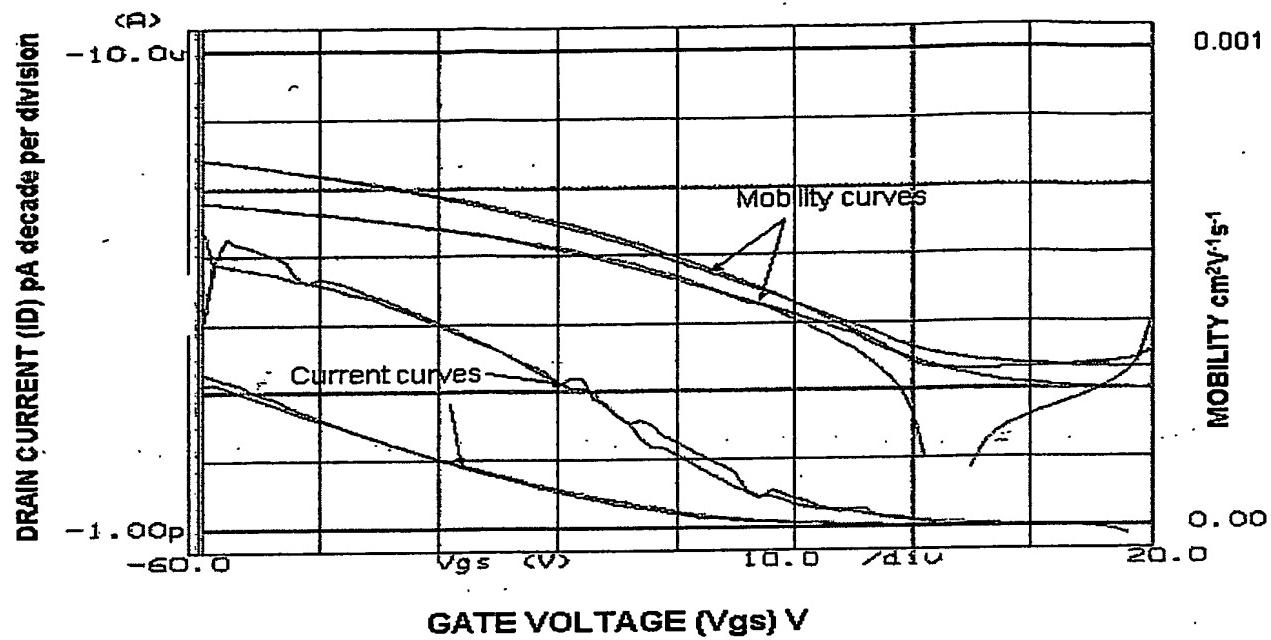
12. A process according to any one preceding claim in which the mixture of the semiconducting material and the substance which results in a Tg of the resulting mixture which is lower than that of the said material is coated onto a substrate as a solution.
- 5      13. A process according to any one preceding claim wherein the ratio of the number of crosslinking groups in the polymer to the total number of monomer units in the polymer is 0.1 to 0.6, preferably 0.2 to 0.3.
- 10     14. A process according to any one preceding claim wherein the amount of said substance in the mixture is at least 25%, preferably at least 40%, and up to 60% by weight of the mixture.
- 15     15. A process in which a multilayer device is produced by forming a first layer which is a cross-linked semiconducting layer on a substrate by a process according to any one preceding claim and forming a second layer on the first layer by solution or suspension deposition of a further layer forming material wherein the first cross-linked semiconducting layer is substantially insoluble in the solvent or suspending medium used to deposit the second layer.
- 20     16. A device which comprises a semiconducting layer produced by a process according to any preceding claim.

ABSTRACT

Semiconducting films are formed on a substrate by coating the substrate with a mixture of a semiconducting material and a substance which results in a Tg of the resulting mixture which is lower than that of the said material, and crosslinking the said material. Multilayer electronic devices may be produced by processes which comprise forming a cross-linked semiconducting film on a substrate in this way and forming a layer on the said film by solution or suspension deposition of a second film forming material in which the cross-linked semiconducting film is substantially insoluble in the solvent or suspending agent used in forming the second film. The invention may be used in making, for example, field effect transistors, light emitting diodes (LEDs), organic solar cells and organic lasers.

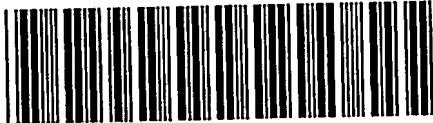


**FIGURE 1: Transfer Curve For Device Comprising Uncrosslinked Formulation**



**FIGURE 2: Transfer Curve For Device Comprising Crosslinked Formulation**

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